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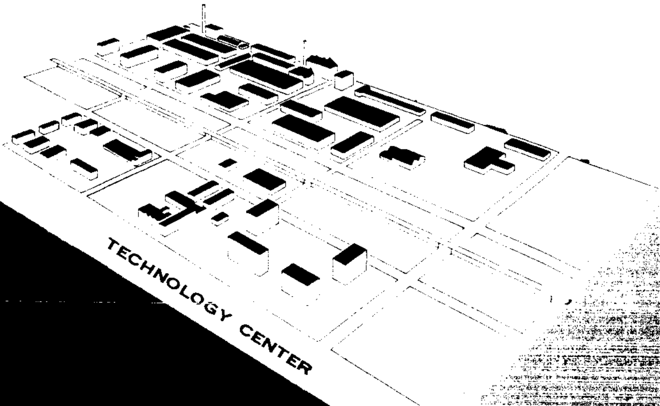

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ARF 1220 - QR 2
(Quarterly Technical Report No. 2)

INVESTIGATION RELATING TO THE
DEVELOPMENT OF CADMIUM TELLURIDE
ENERGY CONVERTERS

National Aeronautics and Space Administration
Headquarters
Office of Propulsion & Power Generation
Code RPP
Washington 25, D. C.
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ARMOUR RESEARCH FOUNDATION
of
Illinois Institute of Technology
Technology Center
Chicago 16, Illinois

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to

National Aeronautics and Space Administration Headquarters
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Code RPP
Washington 25, D. C.

(Covering the Period from 11 October, 1962 to 10 January, 1963)

January 29, 1963

FORWARD

This is the second Quarterly Report on an Investigation Relating to the Development of Cadmium Telluride Energy Converters for the National Aeronautics and Space Administration under Contract Number NASw-455, covering the period October 10, 1962 to January 10, 1963 inclusive. During this period the work has continued to be centered mainly on improvements in the production of crystals suitable for the fabrication of solar cells, supported and guided by electrical and physical measurements. Personnel who have contributed to this report are R. J. Robinson, M. Scott and A. P. van den Heuvel. Data are recorded in ARF logbooks 12753, 12754, 12755.

Respectfully submitted,

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ABSTRACT

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The major developments which have taken place this quarter have resulted from a critical consideration of the conditions which gave rise to the high quality of the accidentally 'cast' single crystal layer which was described in the previous report. This was necessitated by the failure of experiments designed to grow similar layers. It has been found that the magnitude of the cadmium vapour pressure, during zone refining has an adverse effect not only on the production of porous material but also on the tendency of the recrystallized CdTe to stick to quartz surfaces. Reappraisal of all the experiments to date has led to a new method of crystal growth which not only solves the sticking problem but also considerably reduces the possibility of bubble inclusion. In essence, the new technique is simply to perform the zone refining vertically so that any bubbles which do form will rise away from the advancing solid-liquid interface. Furthermore, since only a small surface of the material is exposed to vacuum, sublimation is no longer a problem and the cadmium back pressure is unnecessary. The few boules produced so far have supported these predictions in having highly polished surfaces and being completely free of bubble inclusions despite higher zoning speeds than previously possible. Electrical measurements on samples from the first boule are in progress but have been hampered by the unexpected finding that the material is n-type. Future work is described.

Author

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CADMIUM TELLURIDE ENERGY CONVERTERS

I. INTRODUCTION

This is the second Quarterly Report on an Investigation Relating to the Development of Cadmium Telluride Energy Converters for the National Aeronautics and Space Administration under Contract Number NASw-455, covering the period October 10, 1962 to January 10, 1963 inclusive. The nature of the programme is to investigate the feasibility of utilizing cadmium telluride (CdTe) as a photovoltaic solar energy converter. The objectives of this contract are the construction of experimental cadmium telluride single crystal solar cells and the measurement of their electrical properties.

The work during the second quarter has continued to be centered mainly on improvements in the production of suitable crystals for fabricating solar cells supported and guided by physical and electrical measurements of these crystals.

The main developments during this quarter have been a more complete understanding of the conditions which gave rise to the high quality of the cast sample referred to in the First Quarterly Report, and a new method of single crystal growth as a direct result of this.

The new approach employs a vertical zone refining furnace which was specially constructed for this purpose. So far only a few boules have been prepared due to initial difficulties with the new method. While these have not been single crystal, they did consist of large single crystal areas and were completely free of bubble inclusions which is a considerable improvement over the previous methods. The production of completely single crystal boules now appears to be merely a matter of optimizing the growth conditions such as furnace and zone temperatures and zone speeds for the new furnace.

Electrical measurements on a thin section from one of the boules are in progress but not completed. Indications are that the material is n-type with majority carrier mobilities of roughly the same magnitude as those obtained by de Noble.[1]

The last section is devoted to the directions of future work in the light of the results to date.

II. SINGLE CRYSTAL PREPARATION

A. Introduction

In the first quarterly report mention was made of the accidental production of a cast single crystal layer of CdTe of very much improved electrical and structural quality when compared with that previously obtainable. The structural improvements took the form of freedom from internal bubbles, highly polished surfaces and a high degree of homogeneity. Subsequent experiments, which unsuccessfully attempted to deliberately produce similar layers, were also referred to. The reasons for the failure of these experiments and the 'success' of the accidental casting have been elucidated by a detailed reconsideration of the conditions which gave rise to the high quality of the cast layer. As a result, a totally new approach to the method of growth has been devised and tested and shows considerable promise of success in improving both the quality and the speed of growth of future crystals.

B. The Production of the 'Cast' Single Crystal

The system being employed at the time of the accident consisted of a 12.5 cm quartz boat, containing the cadmium telluride, sealed in an evacuated quartz tube 2.4 cm diameter. A 7 mm quartz tube, sealed axially to the larger tube and containing a small piece of cadmium metal, could be heated independently of the main tube to provide the necessary cadmium vapour pressure over the melt during zone refining to prevent sublimation. This whole system was placed in a horizontal zone refining furnace in which the zone temperature, the temperature gradients and the cadmium temperature could be controlled.

At some time during the experiment some of the liquid CdTe was spilled out of the boat, and became lodged between the side of the boat and the large quartz tube. Due to the particular sizes of boat and tube involved, the spilled material was forced into a thin layer with curved surfaces with its width lying at an angle of roughly 70° to the horizontal.

The significance of this particular configuration did not become apparent until after the experiments described below were found to be unsuccessful in producing single crystal layers.

C. Single Crystal Layer Experiments

Three different approaches to the problem of growing zone refined single crystal layers of cadmium telluride were attempted. All of them were carried out in the horizontal zone refining furnace previously described.

In the first method, a quartz tube of 11 mm diameter was flattened on one side so as to form a 'D' section over about four inches of its length. Small humps were formed in the tube at each end of the flat section to retain the liquid CdTe. Crushed crystals of CdTe were placed in this flat section of the tube, which acted as a boat, and a polished slip of quartz plate, 1/16" thick x 3/8" wide x 4" long was rested on top of the crystals, thus sandwiching them between two quartz surfaces. The tube was then evacuated and sealed as before.

Unfortunately, at the zoning temperatures employed, the flat section of the tube became sufficiently softened to yield under the internal gas pressures.

To obviate against this feature, a new tube was constructed using two quartz slips of the same dimensions as before, the first one being sealed into the tube instead of flattening the tube itself. The other rested on top as before.

In both of these experiments severe sticking of the CdTe to the quartz surfaces was encountered, together with the refusal of the material to form a continuous layer due to surface tension forces. Furthermore, those sections of the semi-layer which could be recovered contained appreciable numbers of bubbles and were polycrystalline.

Finally, to overcome the sticking problem, zone refining was attempted on a CdTe layer contained in a narrow deep slot machined in a cylinder of graphite which just fitted into the quartz tube. Some success with this technique was achieved, but true zone refining was not possible since the graphite, being a good heat conductor, prevented a narrow liquid zone being established with the present furnace. Radio frequency induction heating of the graphite cylinder might overcome this problem and is under consideration. However, the surfaces of the CdTe in contact with the graphite are far from polished so that this method, even if successful, would not be as satisfactory as when quartz is employed. Furthermore, contamination of the CdTe by impurities in the graphite is more likely to be a problem than with a quartz container.

D. Discussion and Explanation of the Foregoing Results

In the light of these experimental results the problems encountered were compared to the conditions which resulted in the accidentally produced cast, and the following explanations were arrived at.

1. The cast layer was thin. The cast material was trapped

between the boat and wall of the tube so that it was squashed into a thin layer. This did not occur in the first two subsequent experiments as the mass of the quartz slip which rested on top of the CdTe was insufficient to overcome the large surface tension forces of liquid CdTe.

2. The cast layer did not stick to the quartz surfaces. It has been found subsequently that the magnitude of the cadmium vapour pressure during the zone refining or melting of CdTe has a significant effect upon the affinity of the solidified material to stick to quartz surfaces. Such behavior is consistent with the fact that cadmium metal, fused under vacuum in a quartz tube, adheres strongly when it solidifies. This is probably due to the formation of oxides by reaction with the silica or traces of oxygen initially present as adsorbed or chemisorbed gas.

During the deliberate experiments, the cadmium pressure was maintained at about 1.5 atmospheres, whereas, in the casting experiment, particular attention was not paid to the cadmium metal temperature as zone width was primarily under investigation. It is now known that the cadmium pressure at the time was in fact probably not more than 0.5 atmosphere. Subsequent experiments, to be described, support this view.

3. The cast layer was single crystal despite a zone speed of 8 mm per minute.

This is a very interesting and important result. When single crystals are to be grown from the melt by the zone refining technique, it has been found that for best results the zone speeds should be as small as possible, and in practice rarely exceed a few cm per hour. Where this is not the case a polycrystalline boule usually results. However, if the direction of growth is very restricted, as is the case with a layer, higher zone speeds are possible.

The reason for this is that only those nuclei initially formed which are favorably oriented, i.e., have their axes oriented such that their maximum growth direction is along the length of the layer, are free to develop, and do so to the exclusion of all the others. This principle is used in all the crystal growth techniques where a seed crystal is not employed. Nevertheless, even with this in mind, single crystal growth at that speed would be rare and appears unlikely, particularly as bubbles were not included in the material. The subsequent experiments tend to support this view.

What appears to have happened in fact is that, although the zone heater speed was large (i.e., 0.8 cm/min), the rate of crystallization within the layer was controlled more by the presence of the boat and its contents than by the movement of the zone heater. Since the large mass of CdTe melt in the boat would not crystallize at the zone speed, the actual rate of crystallization within the layer would be similarly reduced.

4. The 'Cast' Crystal was free of bubbles. One of the most difficult problems encountered by de Nobel and subsequent experimenters in their attempts to grow good quality single crystals of CdTe from the melt by the zone refining technique has been the prevention of bubble inclusions in the recrystallized material. The formation of bubbles occurs when the liquid CdTe has a composition which differs from that of the solid phase which is crystallizing from it. Under these conditions, the excess of the component present in excess is segregated at the solid liquid interface, and since both components of CdTe have a high vapour pressure at the melting point of cadmium telluride, bubble formation will occur. Although these bubbles will tend to rise to the surface, they are easily trapped and built into the solid thereby distorting the lattice and causing the formation of a porous,

polycrystalline material.

It has been shown (de Nobel) that only at the maximum melting point do both the solid and the liquid phases have the same composition, i.e., at stochiometry. This then should be the ideal point for growth to avoid the bubble effect. Unfortunately, however, the vapour pressure at this point is such as to lead to considerable sublimation of the material. For this reason a large back pressure of cadmium vapour is usually applied so that the equilibrium point of the reversible reaction:

$$CdTe_{(Solid)} \rightleftharpoons Cd_{(Gas)} + 1/2\ Te_{2_{(Gas)}}$$

is shifted so far to the left that sublimation is negligible. This necessitates the use of zone speeds of about 5 mm/hr to avoid the bubble effect. These speeds are very restrictive, illustrated by the fact that to zone refine a boule about 6" long 12 times at this speed would take more than two weeks assuming complete automation.

The absence of bubbles in the cast layer, despite relatively high zone speeds may be explained as follows.

Firstly, as mentioned previously, the cadmium pressure was lower than is normally employed so that the composition difference between solid and liquid was less.* Secondly, the width of the layer was at an angle to the horizontal so that the bubbles were free to rise to one side of the layer which was not so in the 'sandwich' type experiments. (Upon examination of the cast it was found that there were some bubbles included along one edge - the upper exposed edge).

* Sublimation would not be serious since only a narrow edge of surface was exposed.

Finally, due to the presence of the boat and its melt on one side, the surface of the cast in contact with the boat would have been the last to freeze so that the bubbles could escape during a substantial part of the solidification. Normally they tend to become trapped under the surface of the boule since the surfaces tend to be the first parts to solidify due to heat loss by radiation.

E. <u>The New Method of Preparation</u>

These considerations have led us to try a completely new approach which has shown considerable success. This is to carry out the zone refining vertically in sealed quartz tubes with a minimum unoccupied volume above the solid and no cadmium back pressure. The advantages of this system, over the conventional horizontal techniques are several.

1. The solid and liquid can be of the same composition, i.e., stochiometric. This is because sublimation can only occur at the top surface which is small, and will be ultimately rejected in any case. Hence bubble formation will be considerably suppressed.

2. By arranging for the zone to move upwards along the tube (or the tube downwards through the hot zone), any bubbles which do form, as a result of slight deviations from stochiometry or volatile inclusions, will rise away from the solidifying interface to the melting interface and thus be extremely unlikely to become trapped in the solid material. This, together with the absence of deliberate cadmium back pressure will improve the stochiometry of the resulting material.

3. Since no cadmium back pressure is deliberately applied, sticking of the solid to the quartz tube will not occur, and polished surfaces will be obtained.

4. The Bridgeman seeding technique can be easily employed by terminating the end of the quartz tube in a point, so that selective nucleation occurs.

5. Zone speed may be increased to the optimum for the material as dictated by thermal conduction etc., instead of being restricted to that necessary to avoid bubble trapping.

All of these predictions have been borne out in practice on boules of about 1 cm diameter by 10 cm long. Typically, zone speeds ranging from 2 cm/hr to 30 cm/hr have been successful in producing dense material with complete freedom from bubble inclusions, and highly polished surfaces which did not stick to the quartz tube. Although they were not completely single crystal boules, they did consist of only a few large crystals and no particular problems are anticipated in producing single crystal material when the conditions are optimised.

This technique should be equally suitable for the production of layer crystals with highly polished surfaces and experiments to this end are planned.

III. ELECTRICAL MEASUREMENTS

The electrical measurements on a thin slice from one of the vertically grown boules of CdTe are not available at present. The delay in obtaining these properties is partly due to the unexpected discovery that this new material is n-type instead of p-type as previously. This fact was not discovered until after the sample had been prepared and silver contacts plated to it. These were found to be non-ohmic in nature and Hall measurements confirmed that the material was indeed n-type. As a result, the experiments